Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process

Li Li [a], Longyu Zhai [a], Xiaoxiao Zhang [a], Jun Lu [b], Renjie Chen [a,*], Feng Wu [a,*], Khalil Amine [b,c,*]

[a] School of Chemical Engineering and the Environment, Beijing Key Laboratory of Environmental Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
[b] Chemical Sciences and Engineering Division, Argonne National Laboratory, IL 60439, USA
[c] Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

HIGHLIGHTS

- Ultrasonic-assisted leaching process is used to recover spent $LiCoO_2$ material.
- Citric acid works better than HCl and H_2SO_4 inorganic acids in the leaching process.
- The mechanism of ultrasonic cavitation on leaching process is explained.
- The recovery process is environmental-friendly, less costly and highly efficient.

ARTICLE INFO

ABSTRACT

The anticipated significant use of lithium-ion batteries (LIBs) for energy storage applications in electric grid modernization and vehicle electrification shall generate a large quantity of solid waste that could become potential environmental hazards and waste natural resources. Recycling of the major components from spent LIBs is, therefore, considered desirable to prevent environmental pollution and to recycle valuable metals. This study reports on the application of ultrasonic-assisted technology to the leaching of cobalt and lithium from the cathode active materials of spent LIBs. Three acids were tested for the leaching process: two inorganic acids (H_2SO_4 and HCl) and one organic acid (citric acid, $C_6H_8O_7 \cdot H_2O$). The results show that the leaching of Co and Li is more efficient with citric acid than with the two inorganic acids. More than 96% Co and nearly 100% Li were recovered from spent LIBs. The optimal leaching conditions were 0.5 M citric acid with 0.55 M H_2O_2, a solid-to-liquid ratio of 25 g L^{-1}, a temperature of 60 °C, leaching time of 5 h, and ultrasonic power of 90 W. The high leaching efficiency is mainly ascribed to the unique cavitation action of the ultrasonic waves. This ultrasonic-assisted leaching process with organic acid is not only effective but also environmentally friendly.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In the current modern economy, an enormous quantity of batteries has been used and disposed of due to the wide application of portable electronic devices such as mobile phones, laptops, and power tools [1]. This number is expected to dramatically increase with the transition to an electrified transportation system, which is already beginning with the advent of hybrid electric vehicles (HEVs) and will accelerate with the introduction of plug-in hybrid electric vehicles (PHEVs) and, ultimately, pure electric vehicles (EVs). Compared with nickel–cadmium (NiCd) or nickel–metal hydride (NiMH) batteries, rechargeable lithium-ion batteries (LIBs) are far more prevalent in consumer electronics [2,3] because of their high energy densities, lack of memory effect, small size, and light weight [4]. With the disposal of these spent electronic products, large quantities of LIB solid wastes are being generated every year. Furthermore, the spent LIBs will not only pollute the environment if they are not disposed of appropriately, but also waste valuable resources if not recycled and reused. Hence, it is imperative to recycle the valuable metals in spent LIBs [5–7].

The most frequently used LIB cathode material is $LiCoO_2$ because of its high energy density, high operating voltage, and good cycling

performance [2,8]. However, it also has some drawbacks, such as high cost, limited cobalt resources, and toxicity [8–10]. In general, the contents of cobalt and lithium in spent LIBs are 5–20 wt. % and 5–7 wt. %, respectively [11,12]. It would be important to recycle the cobalt and lithium from spent LIBs from the viewpoint of resource conservation and environmental protection.

Currently, several approaches have been developed to recycle LiCoO$_2$ from the spent LIBs, including hydrometallurgical [4,13–15], electrochemical [3,6,16,17], and bioleaching [18–20] methods. The hydrometallurgical process is most widely used to recover various metals from spent LIBs by selective precipitation or solvent extraction. A recently proposed alternative involves leaching followed by a sequential selective precipitation, often a liquid–liquid extraction. High extraction of Co and Li has been achieved via leaching with inorganic acids, such as H$_2$SO$_4$ [4,11,15,21–23], HCl [14,24], and HNO$_3$ [25–27]. In our previous work, we investigated different organic acids as alternative leaching agents to avoid the secondary pollution introduced from strong inorganic acids. These organic acids include citric, malic, ascorbic, and aspartic acid [2,8,28,29]. However, the leaching efficiency for valuable metals, such as Co and Li, is low and still needs to be improved.

Ultrasonic agitation has been intensively investigated for extraction of biological samples and plant tissues [30,31]. Swamy et al. [32] and Anjum et al. [33] reported that ultrasonic waves significantly enhance the efficiency of bioleaching of metals from minerals and shale. Marafi and Stanislaus [34] compared the efficiency of ultrasonic and conventional stirring methods for leaching metals from spent hydroprocessing catalysts. Balasubrahmanyam et al. [35] were also able to demonstrate that ultrasonic agitation could enhance the leaching rate of uranium in nitric acid media. However, the application of ultrasonic agitation in the extraction of the metals from spent LIBs has not been studied in detail yet.

In the present work, we applied ultrasonic agitation in the acidic leaching of Co and Li from spent LIBs. The effect of leaching conditions such as temperature, time, agents, and ultrasonic wave power on efficiency was determined. The mechanism of ultrasonic waves in the leaching process was also studied.

2. Experimental

2.1. Reagents, apparatus, and analytical methods

All reagents were of analytical grade and used as received without further purification. Sulfuric acid (H$_2$SO$_4$), hydrochloric acid (HCl) and citric acid (C$_6$H$_8$O$_7 \cdot$H$_2$O) were tested as the leaching agents. Hydrogen peroxide (H$_2$O$_2$) was used as additional reductant with sulfuric acid and citric acid. These acids were supplied by Beijing Chemical Works. Deionized water was used in the preparation of all solutions.

A chemical analysis of the cathodic active material before and after acid leaching was carried out with an X-ray diffractometer (Rigaku, Cu-Kα), and data were collected in the 2θ range of 10–90° at a scan rate of 8° min^{-1}. An FEI QUANTA 6000 scanning electron microscope (SEM) was used to analyze the morphology of the spent LiCoO$_2$ and the leaching residues.

An ultrasonic cleaning machine (KQ-3200 DE, frequency 40 kHz) was used to provide ultrasonic agitation. An inductively coupled plasma atomic emission spectrometer (ICP-AES) was used to determine the concentration of the metals.

2.2. Sample preparation

The spent LIBs were completely discharged to remove the remaining capacity and dismantled. The plastic and steel cases were removed from the cells, and the anodes and cathodes were extracted. The cathodic active materials were easily detached from the supports by immersing the electrode in N-methylpyrrolidone (NMP) for 1 h at 100 °C. After filtering and drying at 120 °C for 24 h, the materials were calcined in a 700 °C muffle for 3 h to eliminate carbon and polyvinylidene fluoride binder. Finally, the materials
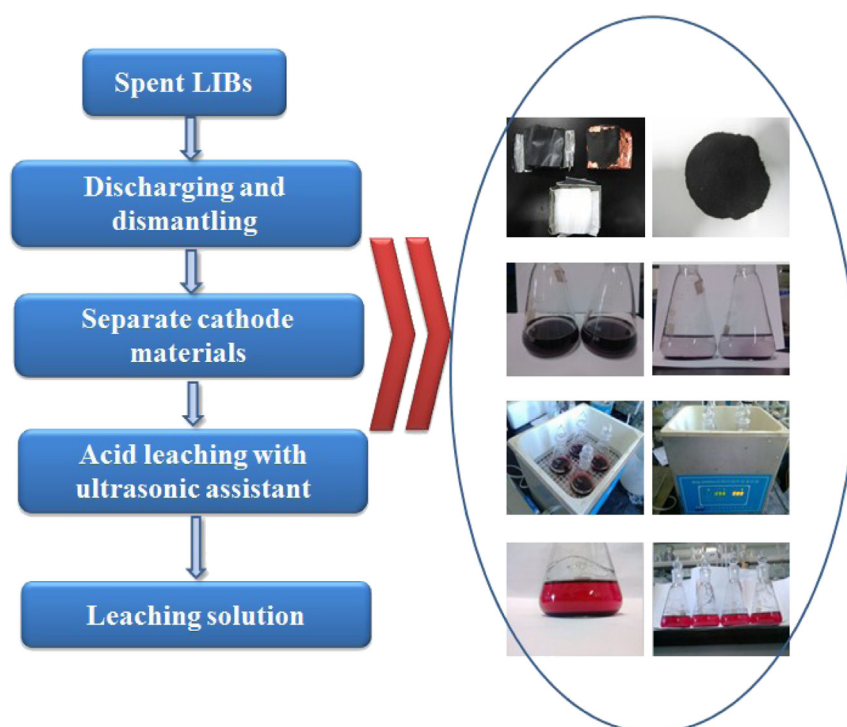

Fig. 1. Illustration of different steps in leaching process for spent LiCoO$_2$.

were grinded using a ball mill for 2 h to decrease the particle size and promote the leaching process.

2.3. Leaching experiments

All of the leaching experiments were conducted in an ultrasonic cleaning machine. In each experiment, 2.5 g cathodic active materials, mainly $LiCoO_2$, from the spent LIBs was mixed with 100 mL selected acid reagent and placed in the ultrasonic cleaning machine (as shown in Fig. 1). The solid-to-liquid ratio was 25 g L^{-1}. Separations were run with different ultrasonic power (60 W, 90 W, and

120 W), leaching time (2 h, 3.5 h, 5 h, and 6 h), and temperature (20 °C, 40 °C, and 60 °C), then the leaching solution was filtered, and the filtrate was analyzed by ICP/AES. The analytical data were used to calculate the leaching efficiency.

3. Results

3.1. Leaching with sulfuric acid

As shown in Fig. 2, the leaching efficiencies of Co in sulfuric acid are much lower than those of Li under the tested conditions with
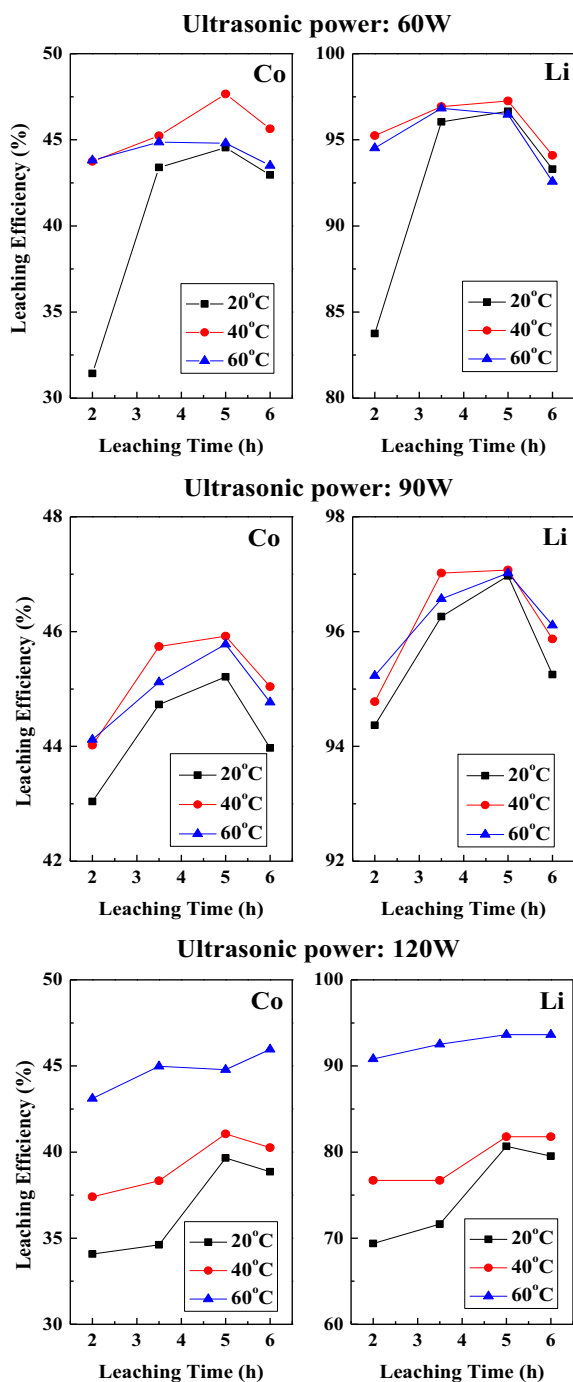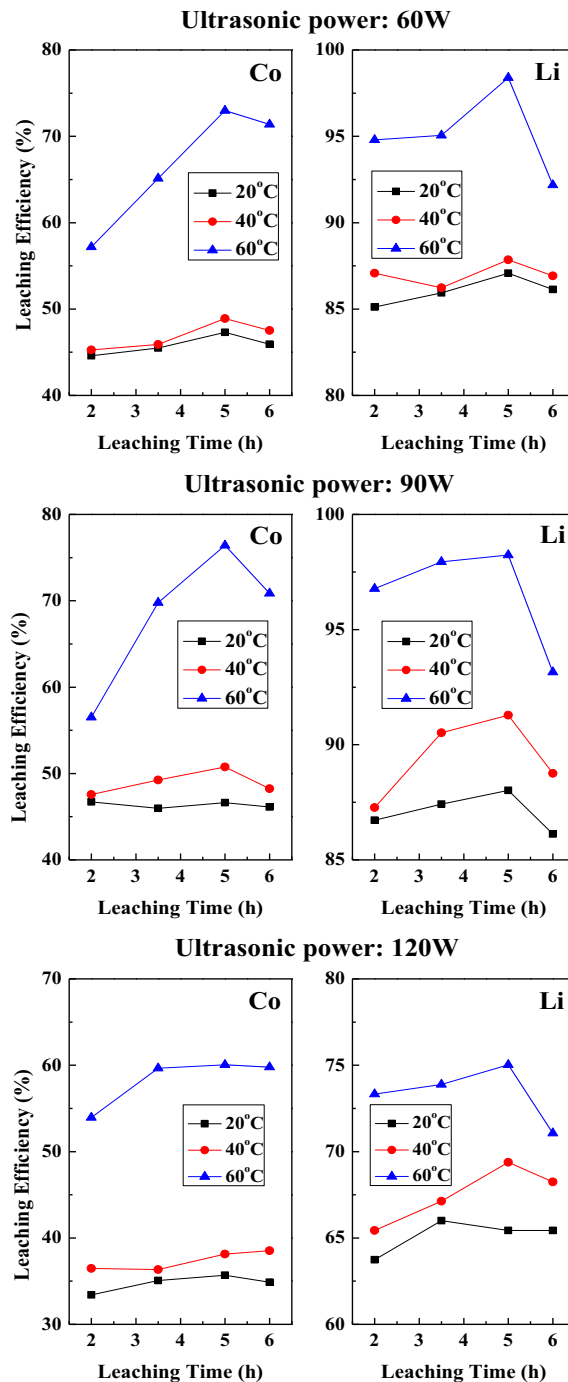

Fig. 2. Effect of leaching temperature (20 °C, 40 °C, 60 °C) and leaching time (2 h, 3.5 h, 5 h, 6 h) on the leaching of spent $LiCoO_2$ with 2 M H_2SO_4 ($H_2O_2 = 0.55$ M, $S/L = 25$ g L^{-1}) at different ultrasonic power (60 W, 90 W, 120 W).

Fig. 3. Effect of leaching temperature (20 °C, 40 °C, 60 °C) and leaching time (2 h, 3.5 h, 5 h, 6 h) on the leaching of spent $LiCoO_2$ with 2 M HCl ($S/L = 25$ g L^{-1}) at different ultrasonic power (60 W, 90 W, 120 W).

different ultrasonic power (60–120 W), leaching time (2–6 h), and temperature (20–60 °C). The highest leaching efficiency of Co is only about 46%–48%, while that of Li reaches up to 97%. In addition, temperature does not significantly affect the leaching efficiency of either Co or Li in sulfuric acid, although the leaching efficiency at 40 °C is slightly higher than that at the other temperatures.

The effect of time on the leaching efficiency of Li and Co is dependent of the ultrasonic power applied. In the case of 120 W, the leaching time showed little impact on the leaching efficiency for both metals. In addition, the leaching efficiency under high power (120 W) appears to be lower than that under lower power

(60 and 90 W). In the sulfuric acid leaching medium, the optimal condition of leaching for both Co and Li is 60 W ultrasonic power, 40 °C temperature, and 5 h leaching time, under which 47.66% Co and 97.25% Li were recovered.

3.2. Leaching with hydrochloric acid

Fig. 3 shows that the leaching efficiency of Co was increased remarkably by use of HCl with the ultrasonic-assisted technology, reaching as high as 76% at 60 °C. At lower temperature (20 and 40 °C), however, the leaching efficiency of Co and Li with HCl was still below 50%. In the 60 °C and 90 W test, the leaching efficiency of Co increased from 56.52% at 2 h to 76.42% at 5 h, and that of Li remained over 95%. Also worth noting is that the leaching efficiency of both Co and Li in HCl was much lower at 120 W compared with 60 W or 90 W. This finding is similar to that with sulfuric acid.

3.3. Leaching with citric acid

Fig. 4 shows that the leaching efficiency of Co and Li in the citric acid increased with time from 2 h to 5 h, but declined from 5 h to 6 h. Generally speaking, the leaching efficiency of Co and Li increased with increasing temperature. Under the condition of 120 W ultrasonic power, the leaching temperature seems to have less effect on the leaching efficiency of Co and Li, compared to the condition of 60 W and 90 W ultrasonic power.

With the ultrasonic power increasing from 60 W to 90 W, the leaching efficiency of Co and Li increased slightly. At 120 W, the leaching efficiency did not improve significantly. Therefore, we selected the optimal leaching conditions in citric acid to be 90 W, 60 °C, and 5 h, which lead to 96.13% Co and 98.4% Li recovered.

3.4. Comparison of leaching with sulfuric acid, hydrochloric acid, and citric acid

The leaching efficiency of Co and Li is summarized in Fig. 5 for the three acids. The results indicate that the leaching of Co depends greatly on the type of acid, with the highest efficiency of 96.13% being obtained with citric acid. Meanwhile, the leaching efficiency of all acids for Li is about the same. A possible explanation for this finding is that the leaching of Li is determined by the concentration of hydrogen ions, which are generated by the dissociation of acid during leaching at the beginning of solid−liquid contact. Thus, the
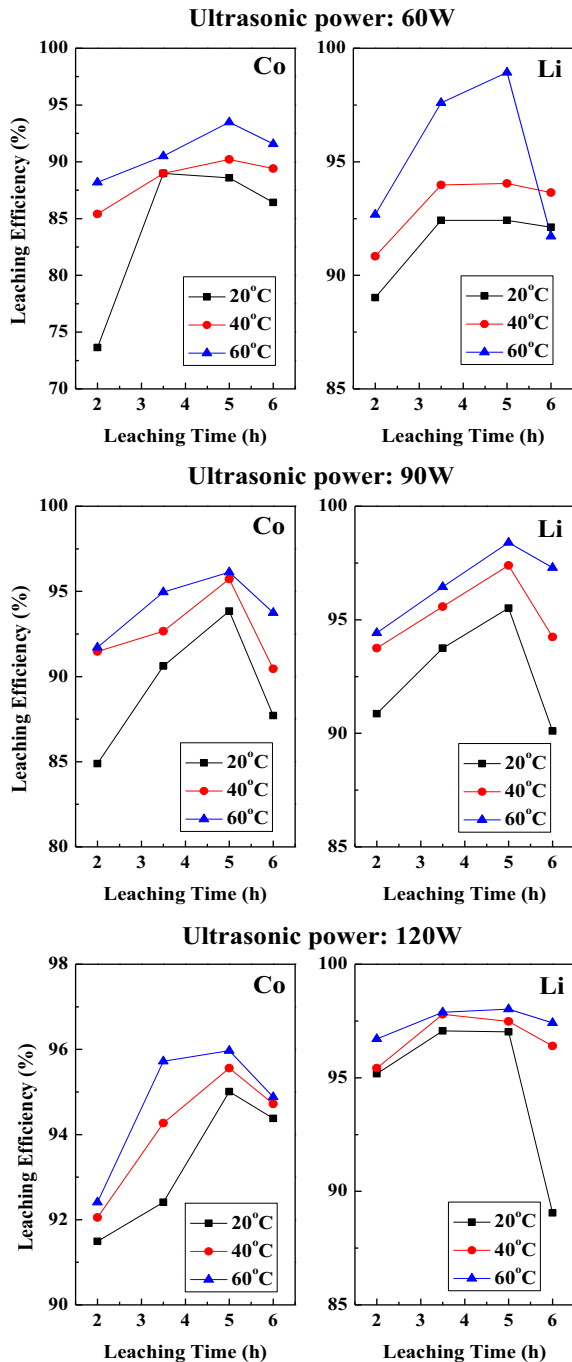

Fig. 4. Effect of leaching temperature (20 °C, 40 °C, 60 °C) and leaching time (2 h, 3.5 h, 5 h, 6 h) on the leaching of spent $LiCoO_2$ with 2 M citric acid (H_2O_2 = 0.55 M, S/L = 25 g L^{-1}) at different ultrasonic power (60 W, 90 W, 120 W).
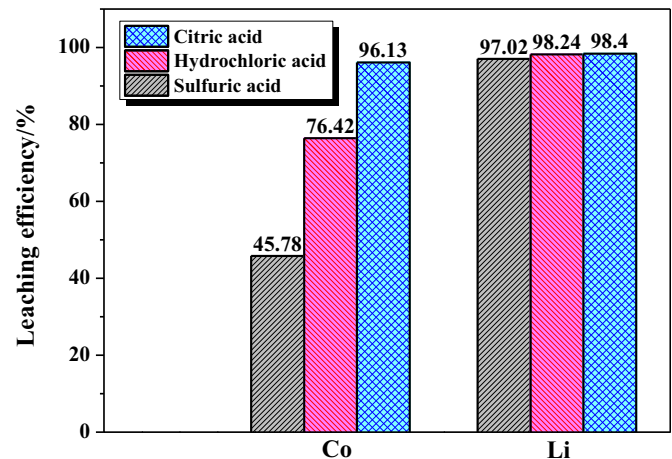

Fig. 5. Leaching efficiency of Co and Li with sulfuric acid, hydrochloric acid, and citric acid (90 W, 60 °C, and 5 h).

dissociation constant of an acid is a crucial factor in determining the leaching efficiency of Li. For citric acid, there are three carboxyls in one molecule and upon dissociation of 1 mol citric acid in distilled water, 3 mol H^+ is theoretically produced. The dissociation constants of citric acid are $K_{a1} = 7.4 \times 10^{-4}$, $K_{a2} = 1.7 \times 10^{-5}$ and $K_{a3} = 4 \times 10^{-7}$, which guarantees the concentration of H^+ as high as strong inorganic acids in the leaching process.

The leaching of Co is influenced both by the concentration of acid and the types of anion in the selected acid. To obtain high leaching efficiency of Co, the high valence of Co should be reduced to a lower state, which could then chelate with the anion readily. The leaching process involves both a dissolution reaction at the solid−liquid interface and the chelation between the metal ion and anion. Citric acid was shown to be one of the best chelating agents, which should accelerate the dissolution process. In our previous work, we have investigated the leaching process of citric acid with $LiCoO_2$ and its possible chelating products. With the addition of reductant H_2O_2 and ultrasonic waves, the chelating reaction between citric acid and Co^{2+} is more favorable and faster, leading to a higher leaching efficiency of Co [4].

The test results showed that for the same test conditions the leaching efficiency of Co and Li by HCl is higher than that of H_2SO_4 due to the different leaching processes. The leaching with H_2SO_4 usually includes the addition of H_2O_2, while HCl by itself could be used as a reductant. Therefore, the leaching process in H_2SO_4 includes two steps: the dissolution of $LiCoO_2$ and the reduction of Co^{3+} to Co^{2+} with H_2O_2. In contrast, the two steps proceed simultaneously with HCl in the leaching process, which promoted the leaching efficiency.

3.5. The mechanism of ultrasonic-assisted leaching

As illustrated in Fig. 6, the ultrasonic-assisted technology played an important role on the leaching of Co and Li. The scanning electron microscopy image in Fig. 6b (right) shows that the spent cathode materials before citric acid leaching contained large secondary particles with irregular morphologies. After the ultrasonic-assisted treatment, the leaching residues showed a much smaller particle size. From X-ray diffraction (XRD) patterns in Fig. 6b (left), the cathode composition of the spent LIBs was $LiCoO_2$, Co_3O_4, and C. At the same time, only Co_3O_4 was present in the leaching residues, indicating that this species was unleachable in citric acid.

Fig. 6a illustrates the mechanism of ultrasonic waves on the leaching of Co and Li from spent $LiCoO_2$. The ultrasonic waves not only promote the convective motion, which increases the contact area of solid and liquid to speed up the leaching efficiency, but also provide a large amount of energy, which facilitates the dissolution of the spent materials. During the negative pressure stage, millions of tiny vacuum holes form in the liquid media, where the gas dissolved in the solution enters the holes and causes a mass of bubbles. This process is called "cavitation". During the positive pressure stage, the cavitation bubbles are crushed with the adiabatic compression process and release a tremendous amount of energy, when the bubbles burst. Thus, a very high pressure (over tens of thousands pounds per square inch), which can help to improve the leaching efficiency, is produced on the interface of the solid and liquid around the bubbles by the tremendous impact of the broken bubbles [36,37]. Compared to inorganic acids of HCl and H_2SO_4, the dissociation of H^+ and chelating with Co^{2+} is greatly accelerated for the citric acid by the cavitation action of ultrasonic. As a
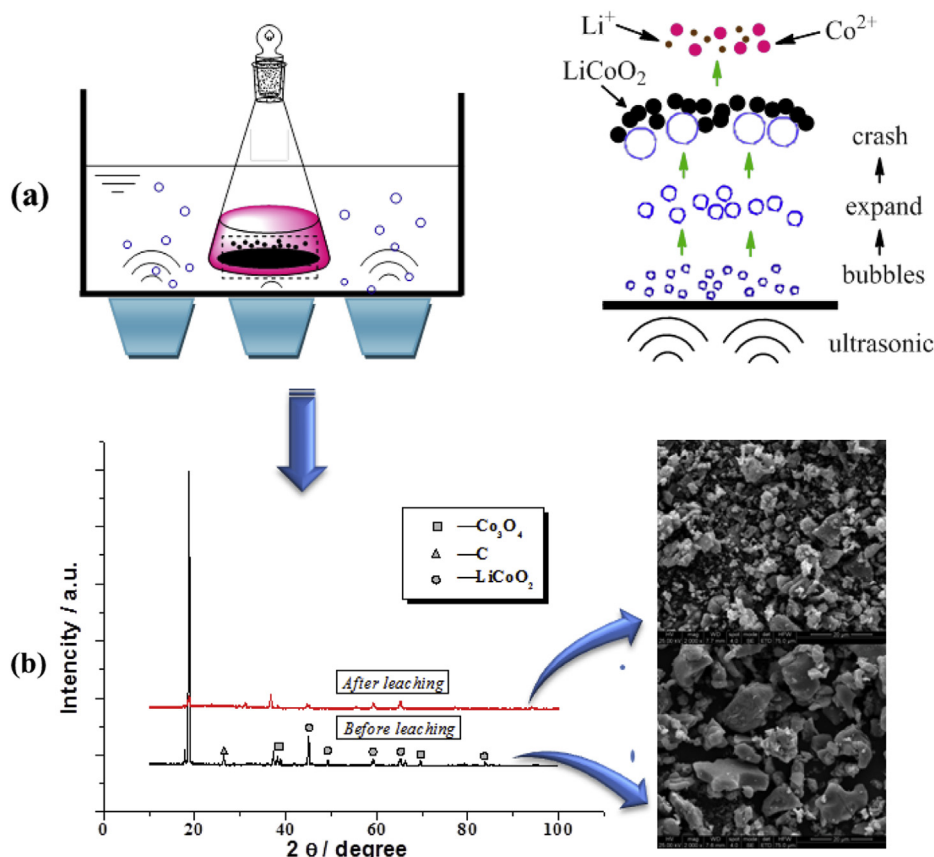

Fig. 6. (a) Mechanism of ultrasonic-assisted leaching of Co and Li from spent $LiCoO_2$ and (b) XRD patterns and SEM images before and after ultrasonic-assisted citric acid leaching.

consequence, with the ultrasonic-assisted technology and citric acid, more than 96% Co and 98% Li present in the spent LIBs were leached at relatively low temperature in a short time.

4. Conclusions

The leaching of Co and Li from spent $LiCoO_2$ with the assistance of ultrasonic agitation was investigated for sulfuric acid, hydrochloric acid and citric acid. The effects of ultrasonic power, leaching time, and temperature on the leaching efficiency were studied in detail. The results showed that citric acid was more effective and environmentally friendly than H_2SO_4 and HCl inorganic acids in the leaching process. More than 96% Co and nearly 100% Li were leached from spent LIBs with the following leaching conditions: 2 M citric acid with 0.55 M H_2O_2, an S/L ratio of 25 g L^{-1}, a temperature of 60 °C, a leaching time of 5 h, and ultrasonic power of 90 W. The application of ultrasonic agitation promoted the leaching efficiency of both metals. The mechanism of ultrasonic cavitation in leaching process was also explained, and the increased leaching efficiency was mainly ascribed to the unique cavitation action of ultrasonic waves.

Acknowledgments

References

[1] R.P. Pamela, C.M. Maiby, H.M.S. Luis, J. Hazard. Mater. 193 (2011) 311–318.
[2] C. Lupi, M. Pasquali, A. Dell'Era, Waste Manag. 25 (2005) 215–220.
[3] B. Swain, J. Jeong, J.C. Lee, J. Power Sources 167 (2007) 536–544.
[4] L. Li, J. Ge, F. Wu, J. Hazard. Mater. 176 (2010) 288–293.
[5] L. Sun, K.Q. Qiu, J. Hazard. Mater. 194 (2011) 378–384.
[6] M.B.J.G. Freitas, E.M. Garcia, V.G. Celante, J. Appl. Electrochem. 39 (2009) 601–607.
[7] M.A. Rabah, F.E. Farghaly, M.A. Abd-El Motaleb, Waste Manag. 28 (2008) 1159–1167.
[8] L. Li, J. Ge, R.J. Chen, Waste Manag. 30 (2010) 2615–2621.
[9] M. Hayashi, M. Takahashi, T. Shodai, J. Power Sources 189 (2009) 416–422.
[10] L. Yang, Q.H. Yan, G.X. Xi, J. Mater. Sci. 46 (2011) 6106–6110.
[11] G. Dorella, M. Mansur, J. Power Sources 170 (2007) 210–215.
[12] O.A. Fouad, F.I. Farghaly, M. Bahgat, J. Anal. Appl. Pyrol. 78 (2007) 65–69.
[13] S.M. Shin, N.H. Kim, J.S. Sohn, Hydrometallurgy 79 (2005) 172–181.
[14] P.W. Zhang, T. Yokoyama, O. Itabashi, Hydrometallurgy 47 (1998) 259–271.
[15] D.P. Mantuano, G. Dorella, R.A. Dorella, J. Power Sources 159 (2006) 1510–1518.
[16] E.M. Garcia, H.A. Taroco, T. Matencio, J. Appl. Electrochem. 42 (2012) 361–366.
[17] E.M. Garcia, J.S. Santos, E.C. Pereira, J. Power Sources 185 (2008) 549–553.
[18] D. Mishra, D.J. Kim, D.E. Ralph, Waste Manag. 28 (2008) 333–338.
[19] B.P. Xin, D. Zhang, X. Zhang, Bioresour. Technol. 100 (2009) 6163–6169.
[20] K.K. Yoo, S.M. Shin, D.H. Yang, Miner. Eng. 23 (2010) 219–224.
[21] A.F. Daniel, M.P. Luisa, M. Daniel, J. Power Sources 187 (2009) 238–246.
[22] J. Kang, J.S. Sohn, H.K. Chang, Adv. Powder Technol. 21 (2009) 175–179.
[23] F.P. Jéssica, G.B. Natália, C.A. Julio, J. Hazard. Mater. 150 (2008) 843–849.
[24] R.C. Wang, Y.C. Lin, S.H. Wu, Hydrometallurgy 99 (2009) 194–201.
[25] C.K. Lee, K.I. Rhee, Hydrometallurgy 68 (2002) 5–10.
[26] S. Castillo, F. Ansart, C. Laberty-Robert, J. Power Sources 112 (2002) 247–254.
[27] V. Ivano, M. Luciano, B. Elena, Waste Manag. 29 (2009) 2332–2335.
[28] L. Li, J. Lu, Y. Ren, J. Power Sources 218 (2012) 21–27.
[29] L. Li, J.B. Dunn, X.X. Zhang, J. Power Sources 233 (2013) 180–189.
[30] S.K. Shu, J.Y. Lee, Q.W. Zhang, Int. J. Miner. Process 74 (2004) S373–S378.
[31] J.L. García, M.D. Luque de Castro, TrAC Trends Anal. Chem. 22 (2003) 41–47.
[32] S. Pereira, L.P. Fonseca, J.L. Capelo, Anal. Bioanal. Chem. 398 (5) (2010) 2315–2324.
[33] K.M. Swamy, K.L. Narayana, N.N. Misra, Ultrason. Sonochem. 12 (2005) 301–306.
[34] F. Anjum, H.N. Bhattia, M. Ghaurib, Hydrometallurgy 100 (2010) 122–128.
[35] A. Balasubrahmanyam, S.B. Roy, S. Chowdhury, Ind. Eng. Chem. Res. 45 (2006) 7639–7648.
[36] G.I. Eskin, Ultrason. Sonochem. 2 (2) (1995) S137–S141.
[37] P. Riesz, D. Berdahl, C.L. Christman, Environ. Health Perspect. 64 (1985) 233–252.